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AN ADSORBED INHIBITOR THEORY FOR BIOFILM—ASSISTED ENNOBLEMENT

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The open circuit potential of titanium in water may significantly vary under illumination. It has been suggested that this shift might have some relation to light effects on oxide film. Experiments were hence, designed to study the effect of illumination on corrosion potential of titanium and platinum in the pond water. The results indicated that the photoelectrochemical and organic photochemical reaction influence on the excursion of potential during day and night hours. Besides, the negative photo-potential were observed for titanium and platinum, indicating the presence of n-type semiconducting film even in presence of biofilm covering the respective surfaces. In addition, the dissolved nutrients within the biofilm were also estimated. It is concluded that "Mixed inhibitor" may strengthen the n-type semiconducting oxide film on these metal surfaces during the processes of ennoblement. The resuts based on these factors are discussed in detail.

Keywords: Open circuit potential, light intensity, semiconducting films, mixed inhibitor and ennoblement.

INTRODUCTION

The ability of marine biofilms to produce an ennoblement (positive shift) of the corrosion potential for stainless alloys is thoroughly documented in literature [1-5]. Dispute, however, continues over the precise bioelectrochemical process which regulates the ennoblement phenomenon. The authors of this paper have suggested that passivity improvement through the action of microbially produced inhibitors could be the major mechanism of ennoblement [5, 6]. This paper attempts to establish the adsorbed inhibitor theory on the basis of biological as well as photoelectrochemical studies.

A photoelectrochemical approach to the ennoblement process appeared worthwhile for many reasons. First, the measurement of photopotential has been widely used in the study of inhibitors and passivity [7]. Second, the principle that photo-induced reactions produce either a positive or negative shift in corrosion potential (depending on the kind of alloy) suggested verification of [8] theory that loss of ennoblement on light-exposed stainless steel specimens was contributed by photosynthetic activity of biofilms. The absence of ennoblement in sunlight - irradiated seawater [9] provided further grounds for photoelectrochemical insights.

In this study, corrosion potential and photopotential measurements were made for titanium and platinum coupons exposed to fresh water, as opposed to sea water employed in the authors' earlier works. The electrochemical study is supplemented by chemical and microbiological analyses of the biofilm.

MATERIALS AND METHODS

All the tests were conducted on grade-2 titanium (UNS* 50250; 50x25x3 mm coupons). Tests were also performed on platinum foils of dimension 50 x 25 x 1 mm. The coupons were pickled in 10% hydrofluoric acid and sulphuric acid respectively (303 K), polished (400 grit), degreased in acetone or trichloroethylene and rinsed in distilled water prior to use. Natural water for biofilm formation was taken from a pond situated within 1 km distance from the corrosion Laboratory in Karaikudi. The pond water had the following characteristics: salinity = 1.5 - 2.2 ppt; temperature = 299.5 - 303 K; *p*H = 8.6 - 9.2 and dissolved oxygen = 4.8 ml l^{-1}.

Open circuit potential measurements

The titanium coupons were exposed to freshly sampled pond water under different light levels in the laboratory (natural, diffuse). The light levels examined were 5,000; 10,000; 20,000 and 30,000 lux (Kyoritsu, model 7200 illuminometer).* The open circuit potentials (OCP) were

* UNS numbers of listed in metals and alloys in the unified numbering system, published by the Society of Automotive Engineers and cosponsored by ASTM.

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recorded at the end of the 1st hour of immersion using an HIL 2605 voltmeter in conjunction with a saturated calomel electrode (SCE).

Periodic recording of OCP was also done for the titanium and platinum coupons exposed in the laboratory. Here, biofilm formation was achieved by renewing the pond water daily. In addition to the natural pond water which contained both bacteria and dissolved organic nutrients (system I), four other test systems were exposed for titanium. System 2 was the pond water passed through 0.2 micron (Millipore) filter to remove the microbiota, while the dissolved organics were retained. System 3 was denatured (boiled) pond water. The boiling procedure ensured destruction of microbiota as well as the dissolved organics. Triple distilled water and 3% NaCl represented systems 4 and 5.

Photoelectrochemical measurements

In all PVC cell (300 ml capacity) was designed to consist of two compartments separated by a thin perforated sheet. This design allowed one electrode (coupon lacqured to obtain 1 cm^2 area of exposure) to be kept in dark while the other could be irradiated through a quartz window. A high power Hg-Xe light source (Ealing, UK; Universal Arc Lamp) was used to illuminate the electrode surface. The term photopotential refers to the potential difference between the illuminated electrode and the other in the dark.

Continuous monitoring of the photopotential was done for titanium exposed to the first four test systems mentioned earlier. Photopotential measurement for platinum was done for system 1 only.

Water and biofilm analysis

Enumeration was done for heterotrophic bacteria, thiosulphate oxidisers and cyanobacteria in the pond water biofilm by using zobell medium, ormerod medium and on medium respectively at the end of 18 days exposure of titanium coupons in room condition.

The nutrient content of the biofilm was analysed at various time intervals (2, 5, 10 and 20 days) after immersion of titanium coupons to natural pond water. The biofilm was scrap-removed and collected in 100 ml of triple distilled water. Nitrite, nitrate, inorganic phosphate and total phosphorous in biofilm samples were estimated following the procedures of Grasshoff et al. [10].

RESULTS

The OCPs measured at the end of the 1st hour of immersion of titanium coupons to natural pond water under differing light conditions are given in Fig. 1. It could be readily inferred that higher the light intensity more active were the OCPs.

Fig. 2 is a plot of OCP vs time for titanium coupons exposed under dark conditions to (a) natual (b) filtered and (c) boiled pond water systems. At the end of 18 days exposure the biofilmed coupons (natural pond water) were ennobled by over 240 mV. An appreciable variation of OCP was not observed, as expected, for coupons exposed to the other two systems.

An appreciable ennobling of titanium (of the order of 180 mV) also occurred in 3% NaCl (Fig. 3). The amount of positive shift in OCP was much reduced, however, for titanium exposed to triple distilled water. In both cases, the OCP remained stable after 7 days, whereas the plateau potential for biofilmed titanium (Fig. 2) was not reached upto 18 days.

Plots of photopotential versus time for titanium in respect of the four systems are given in Fig. 4. Negative photopotentials were observed in all the four systems, indicating the presence of n-type semi-conducting film on the titanium surface. One could also infer from the data that the magnitude of photopotential was much reduced (-15 to -26 mV) in boiled pond water and triple distilled water even after a prolonged period of immersion. Photopotentials were more negative (-58 to -87 mV) in natural and filtered pond water systems. The photopotential in natural pond water showed a continuous increase in the negative direction, though at a small rate.

The OCP for platinum in natural pond water showed uncharacteristic fluctuations throughout the 25 days exposure period (Fig. 5). The amount of ennoblement, in any case, was significant ; the OCP had shifted by nearly 350 mV by the 19th day. The inset in Fig. 5 shows a negative photopotential characteristic for platinum and hence the presence of n-type semiconducting oxide film.

Fig. 6 presents the results of chemical analysis of the biofilm. The nutrient levels showed differing trends steady increase upto 10 days and no major variation thereafter (inorganic phosphate and total phosphorus); an increase upto 10 days and then a sharp decline (nitrate); or an insignificant variation throughout the 20 days period (nitrite). With regard to the speciation of phosphorus, the large difference in value between total phosphorus and inorganic phosphate can be taken to infer that a significant portion of phosphorus remained in the organic state.

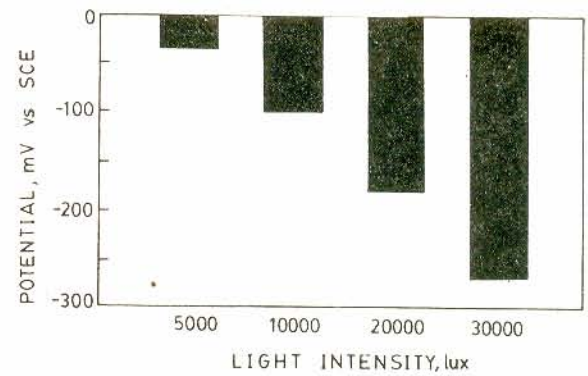


Fig. 1: Corrosion potentials of titanium measured after 1 hour of immersion in freshly sampled pond water under differing light levels in laboratory

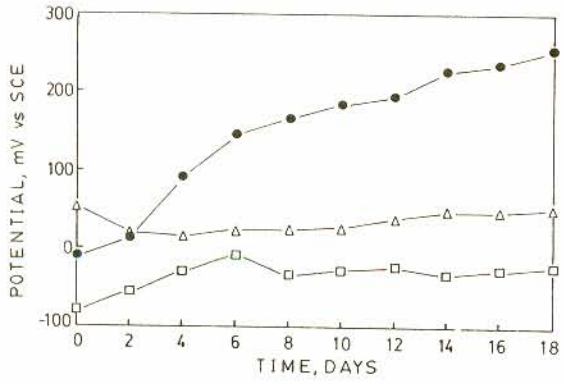


Fig. 2: Corrosion potential vs time plots for titanium exposed to natural (●—●) filtered (△-△) and boiled (□—□) pond water systems

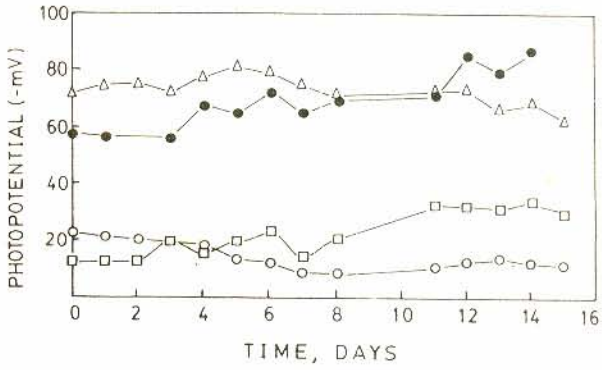


Fig. 4: Photopotential vs time plots for titanium exposed to natural (●—●) filtered (△ – △) and boiled (□—□) pond water systems and triple distilled water (○—○)

Enumeration of biofilm microorganisms showed significantly high numbers of cyanobacteria ($5.7x10^7$ cm^{-2}) as compared to heterotrophs ($5.25x10^5$ cm^{-2}) and thiosulphate oxidisers (3.2×10^3 cm^{-2}) Table I.

DISCUSSION

The present work confirms the earlier observation by Dexter and Zhang [8] that biofilms from pond water are able to ennoble the corrosion potential of alloys similar to the occurrence in seawater. The results (data given in Figs. 1, 4 and 5) are also in accord with the suggestion by Eashwar *et al.* [6] that the fluctuations in corrosion potentials characteristic of alloys exposed to light/dark cycles [8] might result primarily from photoelectrochemical reactions rather than the photosynthetic activity of biofilms.

In the present investigation, the open circuit potential after the immersion of 1 hour varies significantly (the shift being in the negative direction when compared to the OCP in dark) by about 220 mV with increasing light intensity. These results agree with our photopotential observed in the negative direction in presence of biofilm (fresh water system). Hence, these results also explain that the potential shift between day and night hours is due to the influence of light on metal surface by photoelectrochemical reaction not by photosynthesis/respiration of biofilm.

Generally biofilm contains both aerobic and anaerobic bacteria which may contain both acidophilic and alkalophilic bacateria. The major group of cyanobacteria is autotrophic which produce OH^- and H^+ ions in presence of light. During the day time, the other groups like aerobic and anaerobic chemolithoautotrophic of acidophils and acid producing heterotrophs may produce acids which may neutralize the alkaline environment. During night hours, the acid producing heterotrophic group is the only major contributor for the fluctuation of *p*H. Little *et al.* [11] also observed that *p*H of the biofilm in the dark was non-uniform, varying between 5.2 and 9.2 and concluded that the predominance of acidic or basic conditions at the interface may influence the corrosion potential of stainless steel. Further they showed that the *p*H of the biofilm at the metal surface under continuous illumination was only about 8 for Gulf or Mexico waters. This result may be due to the activity of both acidophilic and alkalophilic groups present within the biofilm. Hence, the fluctuation in *p*H during dark period may be due to influence of acidophilic bacteria only. In addition, water may enter in

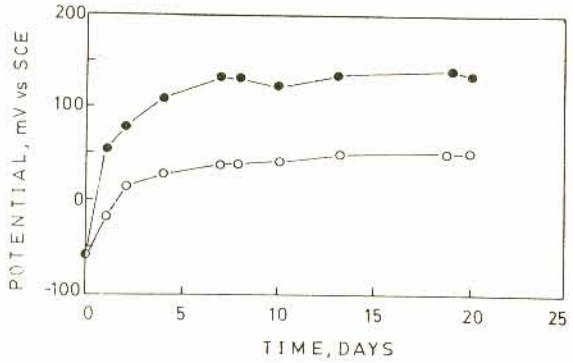


Fig. 3: Corrosion potential vs time plots for titanium exposed to 3% NaCl (●—●) and triple distilled water (○—○) solutions

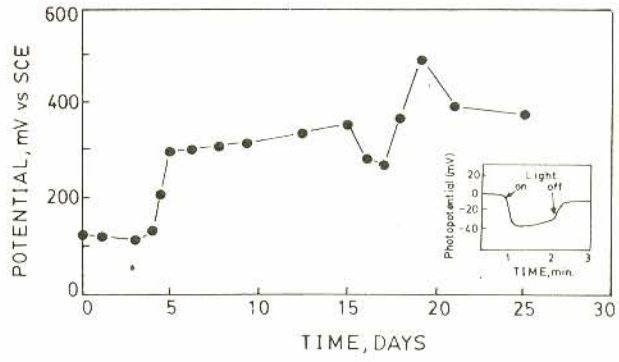


Fig. 5: Corrosion potential vs time plot for platinum exposed to natural pond water. Inset shows photo-response of the biofilmed platinum coupon

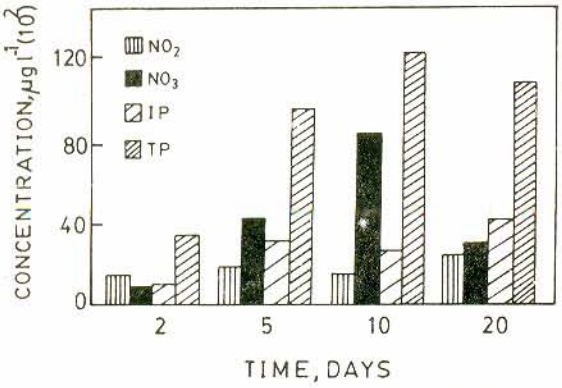


Fig. 6: Levels of nutrients within the biofilm at various time intervals during the exposure of titanium to natural pond water NO_2 NO_3 *IP* *P*

the interstitial space between the bacteria and diatoms which may also try to neutralize the *p*H within the interface.

CONCLUSION

The local *p*H should depend on the presence of bacteria on the metal's surface and does not influence in shifting of potential beteween day and night hours. The present observation also reveals that the light is the major contributor for the fluctuation of potential between day and night.

Since the early works of Oshe and Rozenfeld [12], many investigators have used photopotential as a tool for characterising metal oxides in various electrolyte systems. The photopotential of a metal oxide can be expressed as:

$$VpH = \left(\frac{KT}{\varepsilon}\right) \ln \left(\frac{N_A}{N_D}\right)$$

Where N_A and N_D are the concentrations of acceptor and donor defects respectively, K = Boltzman constant, T = temperature and q = electronic charge. According to this expression, the concentrations of acceptor and donor correspond to those of excessive anions and cations. Thus a semiconducting oxide containing excessive cations (donor) i.e. showing a negative photopotential, is said to be an n-type film. A p-type film is characterised by positive photopotential.

In a general way, the present work confirms the views suggested by earlier investigators [13, 14] that titanium oxide is essentially an n-type semiconducting film.

The smaller amount of negative photopotential in triple distilled water and boiled pond water (Fig. 4) apparently indicates reduced thickness of the oxide film in these systems. The higher magnitude of photopotential in natural and filtered pond water systems may be understood in terms of the strongest light absorbing fraction of organic nutrients.

The present results also explain that the more scattering of open circuit potential between day and night at Tuticorin [6], Delaware waters [15] are due to the influence of light on oxide film and organic nutrients. Mollica *et al.* [16] got less scattering in mediterranean waters because the experiments were conducted in totally dark conditions.

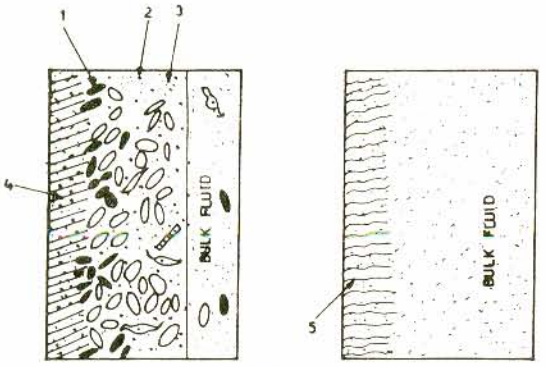
It is well known that organo-compounds of nitrates, polyphosphates and sulphates are efficient pitting inhibitors [17, 18]. Further, Dexter and Zhang [8] have suggested that the production of these chemicals by biofilm bacteria could be one important reason for the remarkable freedom from corrosion of stainless alloy samples ennobled well beyond their stipulated domain of pitting resistance. The present work reports for the first time that the levels of these chemicals (inhibitors) are indeed elevated by biofilm activity (Fig. 6). The authors propose that the nutrients acted as a "mixed inhibitor" which increased the strength of the oxide film [19] and led to enhancement of positive shift. The progressive increase in negative photopotential for the titanium coupon exposed to natural pond water (Fig. 4) lends credence to the authors' suggestion. Althrough one would expect the elevated concentration of adsorbed organics to enhance the oxide layer thickness much more than is reflected in the magnitude of increase of the negative photopotential, the authors presume that the shielding effect of biofilm contributed to the diminished level. This idea is supported by the potential excursion data for titanium exposed outdoors [6] in which the negative shift in day light "(photopotential)" diminished upon ageing of the biofilm.

Data given in Fig. 5 suggest that the oxide film on platinum surface was also an n-type semiconductor. An analysis made by the authors indicates that those alloys characterised by the presence of a p-type semiconductor are not ennobled by biofilms. Examples to this category of alloys include nickel [14] and copper alloys [20] for which no ennobling has ever been observed [21].

A possible model for ennoblement proposed on the basis of the present work is illustrated in Fig. 7. In this model organic nutrients resulting from biofilm activity are expected to

TABLE I: Water/biofilm characteristics of pond water at karaikudi

Place	Salinity water ppt	Temperature K	*p*H	O_2 ml/lit	Biofilm Cyanobacteria	Thiosulphate oxidisers	Heterotrophic bacteria
Amman pond water karaikudi	1.5 to 2.2	299.5 to 303	8.6 to 9.2	4.8	5.7×10^7	3.2×10^3	5.25×10^5



1. Biofilm 2. Suspended solids 3 Dissolved solids

4 Strengthened oxide film 5. Unstrengthened oxide film

Fig. 7: A possible model for ennoblement in which the biofilm and the adsorbed nutrients lead to "strengthening" of the otherwise "normal" oxide film

"strengthen" the porous n-type oxide film and lead to an improvement of ennoblement. The proposed model for ennoblement is consistent with the recent report by Eashwar *et al.* [9] that sunlight irradiation of seawater eliminates the ennoblement causing capacity of biofilms. Spontaneous photodecomposition of dissolved organics [22-24] is a very probable cause for the absence of ennoblement in irradiated seawater. This speculation holds good also for the observations by Subramaniamn [25] that the highly shallow coastal waters of Mandapam have seldom produced an ennoblement on any of the tested alloys. Further work is under way to more convincingly establish the proposed ennoblement theory.

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